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**The Density Behaviour of Heavy Oils in Freshwater:
The Example of the Lake Wabamun Spill**

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Abstract

Bunker fuel oil was spilled into Lake Wabamun, near Edmonton, Alberta, in the summer of 2005. The oil showed peculiar behaviour including submergence, neutral buoyancy, resurfacing and formation of several types of aggregates of oil. Aggregates of oil included the usual tar balls, but also included 'logs', sheets, large lumps and tar balls that sometimes reformed an oil slick. These behaviours and processes are summarized and analysed. Analysis of the oil in the various forms found on the lake show that the density changes were caused by one major process, density changes caused by sediment uptake or loss. The behaviour of the oils is compared in terms of their density behaviour and uptake of various types of sediment.

Introduction

Heavy oils have caused concern recently, particularly because of the increasing frequency of their spillage and because of the difficulty in cleaning them up (NRC, 1999). The International Tanker Owner's Pollution Federation reports that in the past few years 60% of the spills that they

have responded to have been of heavy oils. In early years they rarely had to deal with spills of heavy oils. An NRC study (1999) reports that in the time period 1991 to 1996, 20% of oils spilled in the United States were heavy oils. Of these 20% sank. Sinking occurred in 4% of all spills in that time period.

Heavy oils are also more difficult to study in the laboratory. Often the oils must be heated to place them into the test cells of instruments, then cooled for a long period of time to the test temperature, and then reheated to remove them from the same test vessel. Glassware is difficult to clean as oils are highly adhesive. Oils with high sediment content cannot be analyzed in the same manner as their uncontaminated counterparts. Archimedes displacement methods must be used to measure these densities and these methods have much less accuracy than regular methods.

The phenomena of dense oil behaviour can be divided into sinking, which includes submergence, and over-washing. For the purpose of this paper, sinking is defined as movement below the surface. Over-washing is the washing of a layer of water over the oil while the oil is still close to the surface. The latter is important in that even a micron-layer of water could render the oil undetectable, especially at acute viewing angles, such as from a boat. Over-washing was not observed at Lake Wabamun. The sinking phenomena are reviewed in context of the Wabamun Lake spill in the summer of 2005.

The Wabamun spill occurred on August 3, 2005, when 11 tank cars involved in a train derailment spilled about 800,000 litres of warm Bunker fuel, mixed with some high PAH-containing pole treating oil. The oil ran out of the tank cars and onto lawns of cottages surrounding the Lake, located near Edmonton, Alberta. Figures 1 and 2 show one of many oil paths through the cottage area. The oil quickly entered the lake through many paths along a

broad front of about ½ kilometre. The flow was aided by the fact that the Bunker C had been loaded a few hours before and was still warm and relatively less viscous than it would be later.

Buoyancy Phenomena Observed at Wabamun

Initially, it was believed that all the oil was afloat on the lake, however, very quickly tar balls were observed submerged in the near-shore regions. Within hours, some of the tar balls were showing neutrally-buoyant behaviour, and were seen riding up and down in the water column. Some would rise to the surface, others would be seen sinking to the bottom. The phenomena observed included:

1. One of the unique observations was that the size of the agglomerations varied from the typical 2 to 10 cm tar ball range to massive logs, up to 30 cm in diameter and 5 m in length. A photo of one of these 'tar logs' is shown in Figure 3.
2. Near-shore areas often had tar balls on the bottom of the lake. Typically, the tar balls varied in size from 2 to 10 cm. After high winds, the near shore area could have many of these in the area. Such a situation is shown in Figure 4. A sample of one of the larger of these is shown in Figure 5.
5. The tar balls in this area had a range of densities. Some of them were neutrally buoyant, and moved around in the area, especially when disturbed by water movement.
3. Some near-shore areas had tar mats and similar coverage of oil on the bottom. Such a situation is illustrated in Figure 6. The fate of these was unknown, but it was presumed that much of this oil was driven ashore during higher wind situations.
4. In the reed bed areas tar balls were observed on the bottom. However, during the daytime some of these would rise and create a sheen. Often the tar ball shed oil from several points around its circumference, giving the appearance of a new strange creature. An illustration of one

of these is shown in Figure 7. A view of tar balls sunk in an oiled reed bed is shown in Figure 8. The oil adhered to the reeds also released oil. Tar balls were also seen re-surfacing in areas not in or near reed beds.

5. There were areas, particularly near the spill site, where sheen appeared on the surface.

Although the origin could have been from nearby oiled areas, the persistence of these slicks led some to believe that these slicks were from re-surfacing of sunken oil. Figure 9 shows some of these slicks. A dredge sampling program was carried out in several areas. Some oil on the bottom was found, but only small tar balls and only in the area where slicks appeared as shown in Figure 9. Figure 10 shows one of these tar balls as taken from the dredge sample.

6. Beach re-oiling occurred for many weeks. This is suspected to be largely due to tar mats and tar balls being driven ashore by wind. Some may have been due to oil from re-surfacing, but this would have been a minor contribution.

Analysis of Wabamun Oil Samples

Several samples of oil and oiled material were taken for density analysis. Oil that contained little sediment was analysed by acoustic densitometry (Wang et al., 2004). These samples have an accuracy of about 0.0003%. Results are summarized in Table 1.

Samples of oiled material such as oiled sediment are more difficult to analyse and cannot be put into the glass cell of the acoustic densitometer. These samples were treated in a different manner. First, the density of the entire aggregate was measured gravimetrically employing the Archimedes principle. Second, the sediment was extracted from the oil by filtering and using dichloromethane. The material was dried and weighed to determine the weight percent of sediment. Then, the density of the sediment and other entrained material was measured by the

same Archimedian method. The accuracy of this device is shown along with results in Table 2.

The extraneous material in the tar balls was composed of organic matter primarily grass, similar plant material and some insects; and inorganic material, particularly coarse sediment, coal and some fine sediment.

Explanation for the Buoyancy Behaviour of the Bunker C at Wabamun.

The mechanisms for oil submergence in fresh water include:

1. Evaporation (and other weathering). The Bunker C at Wabamun had a density of about 0.99 g/mL at the lake temperature when spilled. A small amount of weathering would easily change the density to the point where it is greater than that of freshwater.
2. Temperature change. The density of oil does not change at the same rate as does the density of water. Figure 11 shows the density changes of the Wabamun spilled samples and the density changes of freshwater. As it turns out the density of the spilled oil without additional material was sufficient for the Bunker C to remain afloat.
3. Uptake of solid matter, sand and similar granular material particularly, will increase an oil's density. Many spill experiences have shown that only about 2 to 3% sand is necessary to sink oil. It is important to note that the oil flowed over and through land before entering Lake Wabamun and thus may have picked up a lot of sediment in this process. Table 2 shows that the tar balls and sunken samples indeed contained a large amount of extraneous material. Figure 12 shows how little material would be needed to increase the oil density past that density of water. It should be noted that some of the light material in oil would have actually decreased the density of the oil until such material became wetted. This included dry grass and insects, which would have initially entrained air. Thus, wetting of this less dense material and loss of air in the

material becomes another process of density increase leading to submergence.

4. Photooxidation and extreme weathering – certain oils are susceptible to photooxidation which creates a dense crust on the surface of exposed oil. The resulting material is often more dense than water. This is not likely in the case of the Wabamun spill as evidence by the fact that tar balls were seen soon after the spill occurred and not only later as would have been the case if photooxidation were a major factor.

Mechanisms by which oil resurfaces can include:

1. Loss of the solid matter by several means:

A. Break-up of a mat or larger heavy oil body into small particles. The break will occur along the least viscous area – typically where there is less sediment, thus releasing some less buoyant tar balls. It should be noted that the break-up of larger forms of heavy oils usually results in tar balls from about 2 to 100 cm with typical sizes of about 3 to 5 cm. This is a natural and more or less predictable process.

B. Downward movement of particles. If the oil is fluid enough, larger particles such as sand will move to the bottom and ultimately out of the heavy oil mass. At some point the mass becomes less buoyant and starts moving around in the water column and may rise to the surface.

C. Sloughing off of surface. If there is a hard crust with sediment, the ‘crust’ may slough off releasing the less viscous oil inside. This has been observed several times in laboratory experiments when photooxidation hardened the outer surface.

D. Break-through of oil through cracks or fissures in a sedimented or hard layer. Less viscous and buoyant oil can flow (slowly) through any cracks or breaks in outer crusts of tar balls. This occurs in water and even on shorelines.

2. Uptake of lighter material

As noted above, the tar balls would become temporarily less dense if it comes into contact with lighter material such as dry grass, insects, etc. A significant amount of this material was found in the oil.

3. Change in temperatures or salinity

A. Although not highly relevant in the case of Lake Wabamun, the re-surfacing of oil through a change in water density due to salinity or different mineral content, is a frequent occurrence. The density change is typically encountered when the oil rather than the water is transported into a region where the water density is different.

B. Temperature changes – If the oil has a density very near that of water, small changes in temperature (including moving oil or water of different temperatures) can result in oil moving up or down. The temperature and density of some Wabamun samples are shown in Figure 11.

Concluding Remarks

Several interesting oil behaviour phenomena occurred after a spill of Bunker C into a freshwater lake. The formation of a variety of neutrally-buoyant tar balls and larger tar logs were largely caused by the uptake of a variety of extraneous materials including; sand, coal, grass, insects and sediment. The subsequent resurfacing of some of these particles may have largely been due to the loss of sediment or loss of more heavily sedimented portions.

Acknowledgements

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References

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Wang, Z., B.P. Hollebone, M. Fingas, B. Fieldhouse, C. Yang, M. Landriault, and X. Peng, *Characteristics of Spilled Oils, Fuels, and Petroleum Products: I Composition and Properties of Selected Oils*, United States Environmental Protection Agency, EPA/600/R-03/072, National Exposure Laboratory, Atlanta, GA, 2004.

Table 1 Density Measurements on Wabamun Spill Samples

Temp (°C)	Spilled "Bunker C"	Spilled "Pole Treating Oil"	Submerged Oil
0	0.9970	0.9503	1.0356
4	0.9942	0.9474	
5	0.9937	0.9466	1.0334
10	0.9899	0.9430	1.0310
15	0.9867	0.9394	1.0285
20	0.9834	0.9358	1.0259

Table 2 Density of Tar Ball Samples

Sample ID	Sample Density g/mL	Sediment			Proportion		Sediment Density	
		%	Density	RSD (%)	%(wt/wt)	RSD (%)	(g/mL)	RSD
360	1.00	8.5	1.16	2.9	8.5	6.2	1.16	11.7
361	1.01	13.2	1.27	3.0	13.2	4.6	1.27	4.0
369	0.98	3.0	1.14	0.6	3.0	*	1.14	*
376	1.03	11.4	2.13	1.8	11.4	14.5	2.13	1.6
762	1.02	18.4	1.22	0.6	18.4	3.4	1.22	0.7
763	1.00	5.0	1.27	0.7	5.0	3.0	1.27	7.3
764	1.03	7.8	1.00	0.7	7.8	7.0	1.00	10.8
Light Material (Composite)	1.29			4.6				

*Note - single measurement only



Figure 1 One of the several paths taken by the oil to the lake. This may have resulted in uptake of sediment and organic material.



Figure 2 Another of the paths taken by the oil to the lake. This shows that the oil flowed directly over granular material, which may have become incorporated into the oil.



Figure 3 One of several 'tar logs' seen along the shoreline on the downwind side. This particular one is about 2 m long and 8 cm in diameter.

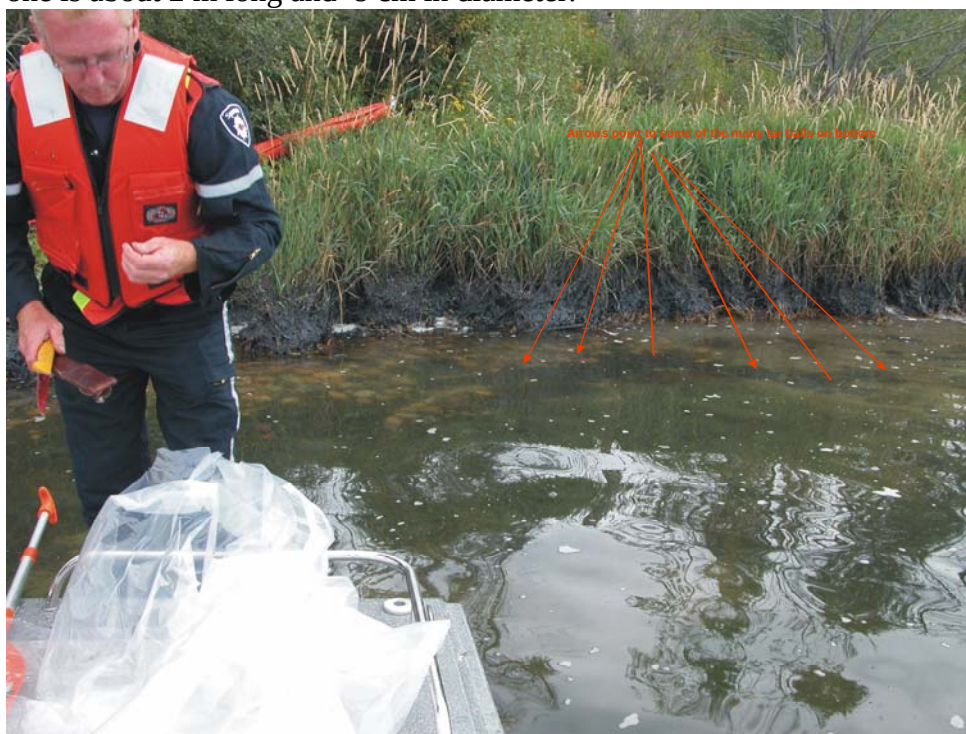


Figure 4 A near-shore zone. The red arrows show some of the many tar balls which cover much of the near shore area. Many of these show a range of densities.



Figure 5 A sample of one of the tar balls taken from the same area as shown in Figure 4.



Figure 6 A near-shore zone. The black areas are all tar mats on the bottom.



Figure 7 A tar ball rising to the surface and releasing sheen.



Figure 8 A near-shore zone with reeds. The round black areas are all tar balls on the bottom.



Figure 9 Sheening occurred in this area down from the original spill site. The origin of the sheens may have been re-surfacing oil as some tar balls were found during a dredge sampling program in the same area.



Figure 10 One of the tar balls in a dredge sample taken in the same area as Figure 9.

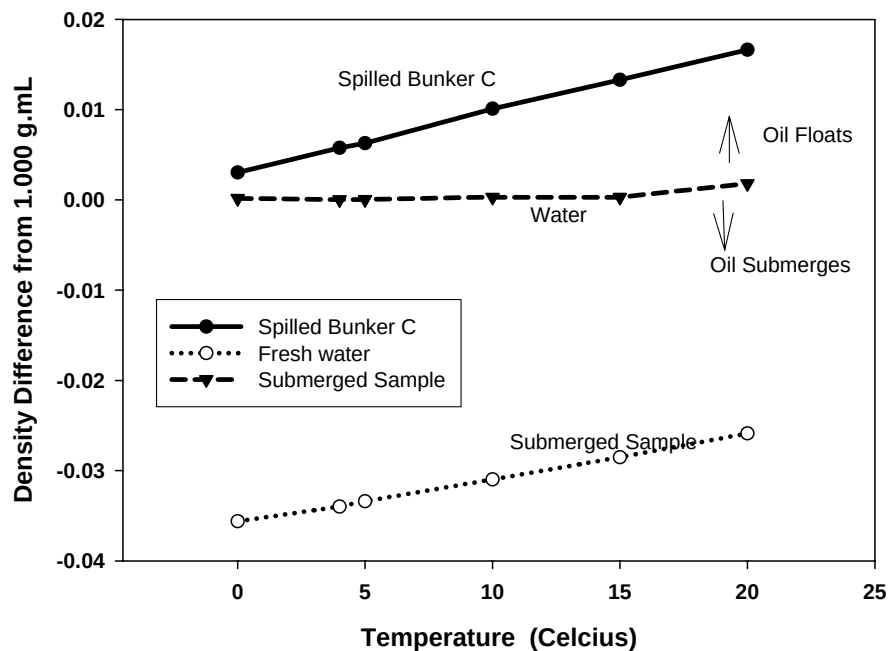


Figure 11 Graph of the density changes of the spilled Bunker C, freshwater and the submerged Bunker C with temperature changes.

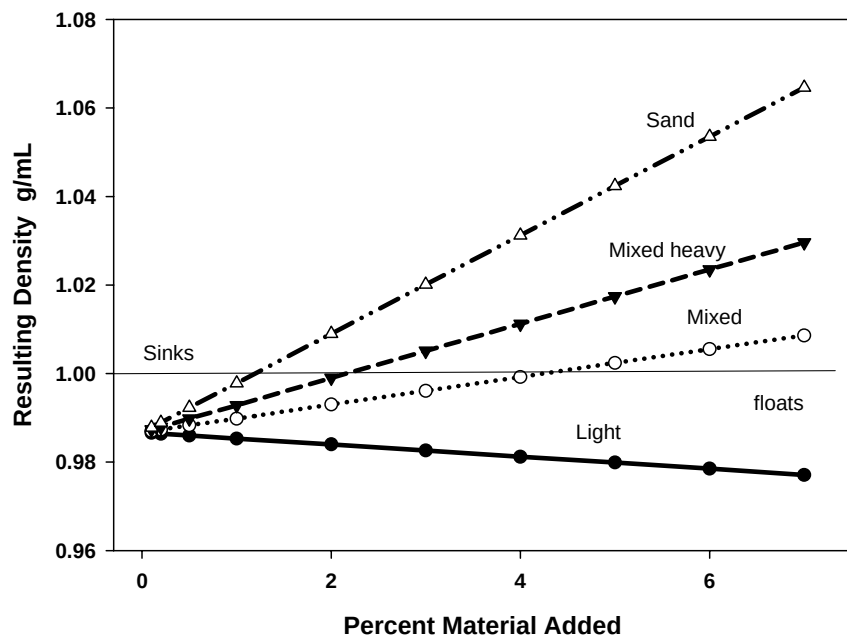


Figure 12 Graph of the density changes by uptake of the various materials found in the tar ball samples.